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Description

The present invention refers to new supported components of catalysts for the polymerization of $\text{CH}_2=\text{CHR}$ olefins wherein R is an alkyl radical with 1 to 4 carbon atoms, or an aryl radical, and mixtures of said olefins with ethylene and the catalysts obtained from said components.

The supported highly active and highly stereospecific catalysts up to now known for the polymerization of propylene and higher olefins, are obtained by the reaction of an Al-alkyl compound partially complexed with an electron donor compound (outside donor) with a solid component comprising a Ti compound and an electron-donor compound (inside donor) supported on a Mg-halide in active form.

Examples of such catalysts have been described in British Patent No. 1,559,194 and Belgian Patent No. 868,682, whereby in British Patent No. 1,559,194 also diethylcarbonate and ethylpivalate are disclosed for the use as outside donor and as inside donor.

Outside donor consisting of silicon compounds containing Si—O—C bonds have been also described (Japanese patent application Sho 79/94590 and Sho 80/36203). Among the various and numerous inside donors also compounds as methyl methacrylate and ethyl pivalate have been cited.

However in all the prior art catalysts in which a silicon compound containing Si—O—C bonds is used as outside donor, esters of benzoic acid and derivatives thereof are used as inside donor.

The performance of the above catalysts, expressed in terms of activity and stereospecificity is not different from the performance of the catalysts in which ethyl benzoate and similar esters of benzoic acid are used as outside donor.

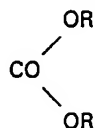
In GB—A—1,452,314 and 1,539,900 there is used a silicon compound as inside donor for the preparation of the catalyst component, whereby in GB—A—1,452,314 the silicon compound has the only function to decompose the adduct $\text{MgCl}_2/\text{donor}$.

It has now unexpectedly been found that it is possible to increase the activity and stereospecificity of the prior art supported catalysts comprising as outside donor a silicon compound containing Si—O—C bonds by using as inside donor an ester having a particular structure.

The catalysts of this invention comprise the product of reaction between the following components:

- a) an Al-trialkyl or an Al-alkyl compound containing 2 or more aluminum atoms linked to each other through oxygen or nitrogen atoms or through SO_4 or SO_3 groups;
- b) a silicon compound containing one or more Si—OR, Si—OCOR or Si—NR₂ bonds (R being a hydrocarbyl radical);
- c) a solid comprising, as essential support, an anhydrous Mg-dihalide present in active form, and supported on said dihalide a Ti-halide or a Ti-haloalcoholate and an electron-donor compound selected from the following groups of compounds:

- 1) Mono and polyesters of saturated polycarboxylic acids wherein at least one of the esteric carbonyl groups is linked to a tertiary or quaternary carbon atom or to a linear or branched chain of at least 4 carbon atoms;
- 2) Mono and polyesters of unsaturated polycarboxylic acids wherein two carboxy groups are linked to vicinal double bond-forming carbon atoms and in which at least one of the R hydrocarbyl radicals of the COOR groups is a branched saturated or unsaturated radical with 3 to 20 C atoms or is an aryl or arylalkyl radical with 6 to 20 C atoms;
- 3) Mono and diesters of aromatic bicarboxylic acids having the COOH groups in ortho position wherein at least one of the R hydrocarbyl radical of the COOR groups contains from 3 to 20 carbon atoms;
- 4) Mono and polyesters of aromatic hydroxy compounds containing at least 2 hydroxyl groups in ortho position;
- 5) Esters of aromatic hydroxy acids wherein at least a hydroxyl group is in ortho position to the carboxy group;
- 6) Esters of saturated or unsaturated carboxylic acids wherein at least one of the hydrocarbyl R and R' radicals of the R COOR' group is a saturated or unsaturated branched radical containing from 3 to 20 C atoms, or is an arylalkyl radical with 7 to 20 C atoms or R is an aryl radical with 3 to 20 carbon atoms linked to the esteric carbonyl group directly or through a methylene group, and in which the R' radical contains from 3 to 20 C when it is a linear hydrocarbyl radical;
- 7) Esters of carbonic acid of formula



in which at least one of the R radicals which can be the same or different are hydrocarbyl radicals with 3 to 20 carbon atoms.

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Representative esters which are suitable in preparing component c) are the following:

Class 1)

diethyl diisobutylmalonate, diethyl n-butylmalonate, diethyl-n-dibutylmalonate, diethylphenylmalonate, diethyl-1,2-cyclohexane-dicarboxylate, dioctylsebacate, diisobutyl adipate.

Class 2)

di-2-ethyl-hexyl-maleate, diisobutylmaleate, diisobutyl-3,4-furan-dicarboxylate, di-2-ethylhexyl-fumarate, 2-ethylhexylmonomaleate.

Class 3)

diisobutyl-2,3-naphthalen-dicarboxylate, di-n-propyl, di-n-butyl, diisobutyl, di-n-heptyl, di-2-ethylhexyl, di-n-octyl, di-neopentyl phthalates, monobutyl and monoisobutyl esters of phthalic acid, ethyl-isobutyl-phthalate, ethyl-n-butyl-phthalate.

Class 4)

2,3-diacetoxynaphthalene, 1,2-diacetoxybenzene, 1-methyl-2,3-diacetoxybenzene.

Class 5)

Benzoyl-ethylsalicylate, acetyl-methylsalicylate.

Class 6)

Ethylene-glycol-pivalate, 1,4-butanediol-pivalate, benzyl and isobutylpivalate, n-propylpivalate, ethyl diphenylacetate, isobutylmethacrylate, isobutylacrylate, ethylbenzoylacetate, isobutylpyruvate, isobutyl-trans-3-methoxy-2-butenate.

Class 7)

phenyl-ethylcarbonate, diphenyl carbonate.

Preferred compounds are the esters of maleic, pivalic, methacrylic, carbonic and phthalic acids.

As indicated, the esters of the polycarboxylic acids can contain beside the ester groups also unesterified COOH groups.

In preparing component c) the esters are contacted with the active Mg dihalide or the precursors of said dihalides as preformed compounds or the esters can be formed in situ by means of known reactions as for instance by esterification between an alcohol or an alcoholate and an aryl halide or between an anhydride or an hemiester of a polycarboxylic acid with an alcohol or by transesterification. The esters can be also used in mixture with other known inside donors.

The active anhydrous Mg dihalides forming the essential support of component c) are the Mg dihalides showing in the X-ray powder spectrum of component c) a broadening of at least 30% of the most intense diffraction line which appears in the powder spectrum of the corresponding dihalide having 1 m²/g of surface area or are the Mg dihalides showing a X-ray powder spectrum in which said most intense diffraction line is replaced by a halo with the intensity peak shifted with respect to the interplanar distance of the most intense line and/or are the Mg dihalides having a surface area greater than 3 m²/g.

The measurement of the surface area of the Mg dihalides is made on component c) after treatment with boiling TiCl₄ for 2 hours. The found value is considered as surface area of the Mg dihalide.

Very active forms of Mg dihalides are those showing a X-ray powder spectrum in which the most intense diffraction line appearing in the spectrum of the corresponding halide having 1 m²/g of surface area is decreased in relative intensity and broadened to form a halo or are those in which said most intense line is replaced by a halo having its intensity peak shifted with respect to the interplanar distance of the most intense line. Generally the surface area of the above forms is higher than 30—40 m²/g and is comprised in particular between 100—300 m²/g.

Active forms are also those deriving from the above forms by heat-treatment of component c) in inert hydrocarbon solvents and showing in the X-ray spectrum sharp diffraction lines in place of the halos.

The sharp, most intense line of these forms shows in any case a broadening of at least 30% with respect to the corresponding line of the Mg dihalide having 1 m²/g of surface area. Preferred Mg dihalides are Mg dichloride and Mg dibromide. The content in water of the dihalides is generally less than 1% by weight.

For Ti halides or Ti haloalcoholates and esters supported on active Mg dihalide is meant the above compounds which may be chemically or physically fixed on the support, not extractable from component c) by treatment of the same with boiling 1,2-dichloroethane for 2 hours.

Components a), b) and c) are made to react each other in any order; preferably, however, components a) and b) are premixed before being contacted with component c).

Component c) may be premixed with either component a) and/or b). The pre-mixing of a) and b) is conducted at temperatures comprised, usually, between room temperature and the temperature used in the polymerization process.

The pre-reaction of c) and b) may be carried out also at higher temperatures. Compound b) may be also

incorporated and made to react with component c) itself. Component b) is made to react in a molar ratio with respect to the halogenated Ti compound supported on component c) of at least 1 and in a molar ratio with respect to the Al-alkyl compound used as component a) of less than 20 and preferably comprised between 0.05 to 0.3.

- 5 In component c) the molar ratio between the Mg dihalide and the halogenated Ti compound supported therein is comprised between 1 and 500 and the molar ratio between said halogenated Ti compound and the electron-donor supported on the Mg dihalide is comprised between 0.1 and 50. The silicon compounds set forth in b) include compounds of general formula:



wherein:

R is an alkyl, alkenyl, aryl, arylalkyl, cycloalkyl radical with from 1 to 20 carbon atoms;

Y is a —OR', —OCOR', —NR₂' wherein R', either equal to or different from R, has the same meaning as

- 15 R;

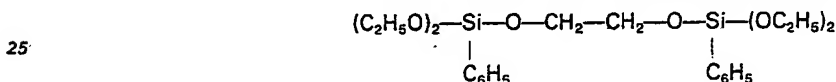
X is either a halogen or hydrogen atom or a —OCOR'', —NR₂'' group wherein R'', either equal to or different from R', has the same meaning as R';

m, n and p are numbers comprised respectively between:

m between 0 and 3, n between 1 and 4 and p between 0 and 1; and m+n+p is equal to 4.

- 20 Other silicon compounds that may be used are compounds in which two or more silicon atoms are bound to each other through oxygen or nitrogen atoms.

Examples of these compounds are hexaethoxydisiloxane, symmetrical diphenyltetraethoxydisiloxane



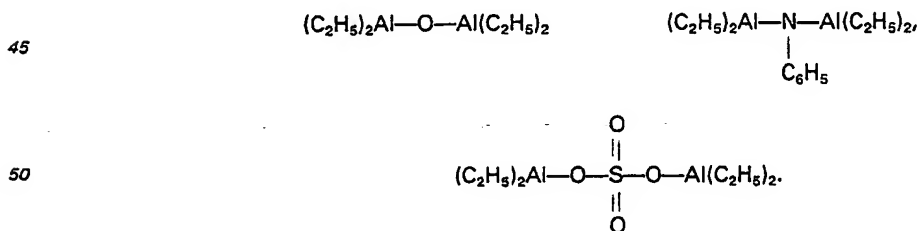
- Preferred silicon compounds are: phenylalkoxysilanes as phenyltriethoxy or trimethoxysilane, diphenyldimethoxy and diethoxysilane, monochlorophenyldiethoxysilane; alkylalkoxysilanes as ethyltriethoxysilane, ethyltriisopropoxysilane.

- Examples of other suitable compounds are: chlorotriethoxysilane, acetoxyltriethoxysilane, vinyltriethoxysilane, butyltriethoxysilane, triphenylmonoethoxysilane, phenyltricycloethoxysilane, phenyldiethoxydiethylaminosilane, tetraphenoxysilane or tetraalkoxysilanes as tetramethoxysilane.

- 35 The silicon compound can be also formed in situ by reaction for instance of a halogenated silicon compound as SiCl₄ with an alcohol or an alcoholate of Mg or Al.

- In the catalysts of the invention the silicon compound is present in a combined form in the solid product of the reaction between the various catalyst-forming components, in a molar ratio between the silicon compound and the halogenated Ti compound greater than 0.05 and generally comprised between 0.1 and 5.

- 40 The Al-alkyl compounds forming component a) includes Al-trialkyls as for instance Al-triethyl, Al-triisobutyl, Al-triisopropyl and compounds containing two or more Al atoms linked to each other through hetero-atoms as:



- As indicated Al-alkyl compounds in which Al atoms are linked through groups as SO₄ or SO₃ are also suitable.

The Al-alkyl compounds may be used in mixture with Al-alkyl halides as AlEt₂Cl.

- Component c) is prepared according to known methods. One of these methods consists in co-milling the Mg halide and the electron-donor compound of this invention until the appearance in the X-ray spectrum of the milled product of the modifications above set forth for the spectrum of the Mg dihalide and thereafter reacting the milled product with the Ti-compound.

Preparations of this type are described in British Patent No. 1,559,194.

Similar preparations are described in U.S. Patents Nos. 4,107,413, 4,107,414 and 4,107,415.

- Another method consists in reacting the adduct of a Mg halide with an alcohol, with a Ti compound in the presence of an electron-donor compound not containing active hydrogen atoms. This method is described in Belgian Patent No. 868,682.

According to another method, which is described in published German application 3,022,738, the adduct between the Mg dihalide and the alcohol is reacted in liquid form with the halogenated Ti compound and the electron-donor compound.

Further methods are described in published German application 2,924,029, U.S. Patent 4,220,554 as well as in Italian Patent Application No. 27.261/79.

Another method consists in co-milling the Mg dihalide, the halogenated Ti compound and the electron-donor compound until activation of the Mg dihalide and in treating a suspension of the milled product in a halogenated hydrocarbon as 1,2-dichloroethane, chlorobenzene, methylene chloride, hexachloroethane.

The treatment is carried out at temperatures comprised between 40°C and the boiling point of the halogenated hydrocarbon for a time ranging in general from 1 to 4 hours.

According to another method a porous support like SiO_2 or Al_2O_3 , having a low content of OH groups (preferably less than 1% by weight) is impregnated with a liquid adduct between the Mg dihalide and an alcohol; the support is then treated with an excess of TiCl_4 containing dissolved the electron-donor compound according to the procedure described for instance in German patent application 3,022,728 or Belgian patent 868,682.

In all the above methods the final product contains a Mg dihalide, present in the active form as set forth here above.

Other known methods which lead to the formation of Mg dihalide in active form or to Ti-containing Mg dihalide supported components, in which the dihalide is present in active form, are based on the following reactions:

- reaction of a Grignard reagent or a Mg R_2 compound (R being a hydrocarbyl radical) or complexes of said Mg R_2 compounds with Al-trialkyls, with halogenating agents as AlX_3 or $\text{Al R}_m\text{X}_n$ compounds (X is halogen, R is a hydrocarbyl $m+n=3$), SiCl_4 or HSiCl_3 ;
- reaction of a Grignard reagent with a silanol or polysiloxane, H_2O or with an alcohol and further reaction with a halogenating agent or with TiCl_4 ;
- reaction of Mg with an alcohol and a halogenidric acid or of Mg with a hydrocarbyl halide and an alcohol;
- reaction of MgO with Cl_2 or AlCl_3 ;
- reaction of $\text{MgX}_2 \cdot n\text{H}_2\text{O}$ (X=halogen) with a halogenating agent or TiCl_4 ;
- reaction of Mg mono or dialcoholates or Mg carboxylates with a halogenating agent.

The Ti-halides or Ti-halogenalcoholates, include in particular the Ti-tetrahalides, Ti-trihalides and Ti-trihalogenalcoholates. Preferred compounds are: TiCl_4 , TiBr_4 , 2,6-dimethylphenoxytrichlorotitanium.

The Ti-trihalides are obtained according to known methods, for instance by reduction of TiCl_4 with Al or a metallogenic Al compound or with hydrogen.

In case of the Ti-trihalides it may be convenient for the purpose of improving the performance of the catalysts to carry out an oxidization, even if partial, of the titanium, either during or after the preparation of component c).

To this purpose there may be used halogens, iodine halides.

Preferred catalysts are those in which: component c) is obtained from MgCl_2 , TiCl_4 and esters of maleic, pivalic and phthalic acids and in which component b) is phenyl or ethyltriethoxysilane or diphenyldimethoxy or diethoxysilane.

Component a) is an Al-trialkyl as Al-triethyl or Al-triisobutyl.

Component c) is prepared according the methods described in Brit. Pat. No. 1,559,194, Belgian patent No. 868,682, published German application No. 2,924,029, U.S. Patent 4,220,554, Italian Pat. Appln. 27,261/79 or published German application 3,022,738.

The preferred method of preparing component c) includes also the co-milling of MgCl_2 , TiCl_4 and the ester and in treating the milled product with a halogenated hydrocarbon as 1,2-dichloroethane.

The catalysts according to the invention are used to polymerize the alpha-olefins according to known methods that is, in carrying out the polymerization in a liquid phase, either in the presence or absence of an inert hydrocarbon solvent, or in gas phase or also by combining, for instance, a liquid phase polymerization step with a step in gas phase.

In general the temperature is comprised between 40° and 160°C, but preferably between 60° and 90°C, operating either at atmospheric or at greater than atmospheric pressure.

As a molecular weight regulator hydrogen or other regulators of a known type are used.

The catalysts are used particularly suitable in polymerizing propylene, butene-1, styrene, 4-methylpentene. The catalysts may also be used according known methods to polymerize mixtures of propylene and ethylene to form modified polypropylenes having better shock-resistance at low temperatures (the so called block copolymers of propylene and ethylene) or to obtain random crystalline copolymers of propylene with minor proportions of ethylene.

The following examples are given for merely illustrative purpose and are not intended to be in any way limiting the scope of the invention.

Examples 1—10

Into a stainless steel autoclave having a total volume of 30, equipped with a magnetical stirrer and a thermocouple heat-stabilized at 60°C and kept under pressure by a nitrogen atmosphere, there were introduced 1000 ml of a suspension in degassed and anhydrous n-heptane containing 5 m mols of triethylaluminum, the phenyltriethoxysilane (PES) and a solid catalytic component prepared according to example 1 of Italian Pat. Appln. 27.261/79, but using, instead of ethylbenzoate, the esters listed in Table I, while propylene was also fed in. The catalytic components thus prepared showed X-ray powder spectra in which the most intense diffraction line appearing in the spectrum of MgCl_2 having $1 \text{ m}^2/\text{g}$ of surface area is decreased in relative intensity and broadened to form a halo.

The autoclave was closed and thereafter hydrogen was introduced up to a pressure of $0,2 \cdot 10^5 \text{ Pa}$, the temperature was brought to 70°C and simultaneously, propylene was introduced up to a total pressure of $7 \cdot 10^5 \text{ Pa}$.

During the polymerization the pressure was kept constant by continuous feeding of the monomer. After 4 hours, the polymerization was stopped by quick cooling and degassing of the polymeric slurry. The polymer was separated from the solvent by filtering and was dried in a hot nitrogen flow at 70°C. The quantity of polymer dissolved in the filtrate was thereupon isolated, weighed and summed to the polymer soluble in boiling n-heptane, for the calculation of the isotacticity index (I.I.).

The quantity of catalytic component used and the content of Ti in said component, the molar ratio of the phenyltriethoxysilane with respect to the triethylaluminium, the yield in polymer with respect to the introduced catalytic component, the isotacticity index (I.I.), the surface area of the solid catalytic component and the inherent viscosity determined in tetralin at 135°C, are reported in Table I.

Example 11

Example 8 was repeated under the same polymerization conditions described in Examples 1—10, but using a solid catalytic components prepared according to Example 7 of German Pat. Appln. 2.643.143.

The catalytic component showed a X-ray powder spectrum in which the most intense diffraction line appearing in the spectrum of MgCl_2 having $1 \text{ m}^2/\text{g}$ of surface area is decreased in relative intensity and broadened to form a halo. The content of Ti in the solid catalytic component, the quantity of said component, the molar ratio between triethylaluminium and PES, the results of the polymerization test are reported in Table I.

Example 12

The solid catalytic component prepared according to Example 11 was suspended in the inert hydrocarbon solvent Isopar G (a mixture of isoparaffinic hydrocarbon boiling in the temperature range of from 158° to 172.5°C) and heat-treated at 120°C for 24 hours. The catalytic components thus obtained showed a X-ray powder spectrum in which the most intense diffraction line appeared as a sharp line, the half peak breadth of which however was broadened more than 30% the corresponding half peak breadth of MgCl_2 having $1 \text{ m}^2/\text{g}$ of surface area.

The catalyst component obtained was used under the same polymerization conditions described in Example 11.

The characteristics of the solid catalytic component, the results of the polymerization test are reported in Table I.

Comparative Examples 1 and 2

Example 1 was repeated but using the solid catalytic component prepared according to example 1 of Italian Pat. Appl. No. 27,261/79. The X-ray powder spectrum was similar to that of the catalytic component of Example 1.

The results of the polymerization tests have been reported in Table I.

Comparative Example 3

Example 11 was repeated except that the solid catalytic component prepared according to Example 7 of German Pat. Appln. 2,643,143 was used. The X-ray powder spectrum was similar to that of catalytic component of Example 11. The results of the polymerization tests have been reported in Table I.

Examples 13—18

Example 1 was repeated using a solid catalytic component prepared as follows.

Anhydrous MgCl_2 , an ester, listed in Table II, and TiCl_4 in molar ratio of 1:1 with respect to the ester, were co-ground in a vibrating mill of the type VIBRATOM manufactured by N. V. TEMA'S, Gravenhage (Holland), having a total volume of one liter and containing 3 kg of stainless steel balls of 16 mm diameter.

Grinding was effected for 72 hours employing a filling coefficient equal to 100 g/l of total volume (vacuum), at an interior temperature of the mill of 25°C.

Charging of the mill, the grinding and discharging of the mill occurred in a nitrogen atmosphere.

10 g of the co-ground product was contacted with 100 ml of 1,2-dichloroethane at 80°C for 2 hours. After this period, 1,2-dichloroethane was removed by filtration at 80°C and the residual solid product

was repeatedly washed with n-heptane at room temperature till the disappearance of the chlorine ions from the filtrate and then was kept in heptanic suspension.

The catalytic components thus prepared showed a X-ray powder spectrum in which the most intense diffraction line appearing in the spectrum of $MgCl_2$ having $1 \text{ m}^2/\text{g}$ of surface area was decreased in relative intensity and broadened to form a halo.

The type of ester, the characteristics of the solid catalytic component, and the results of polymerization tests have been reported in Table II.

Examples 19—26

Example 1 was repeated but using a solid catalytic component prepared according to Example 3 of Italian Paten Appln. No. 26,908 A/78.

A solid adduct $MgCl_2 \cdot 2.5 C_2H_5OH$ in the form of spherical particles were slowly added to a suspension of an adduct $TiCl_4$ -ester using molar ratios $Mg/ester$ of 10 and $TiCl_4/C_2H_5OH$ of 10.

The whole was then heated at 100°C , kept at said temperature for 2 hours and then filtered at 100°C . The resulting solid product was treated with 110 ml of $TiCl_4$ at 120°C for 2 hours. After this period, $TiCl_4$ was removed by filtration and the solid was then washed with n-heptane at temperatures decreasing from 90°C to room temperature until the chlorine ions disappeared from the filtrate and then kept in heptanic solution.

The catalytic components thus prepared showed the same X-ray spectra similar to those of the catalytic component of Examples 1—10.

The esters, the characteristics of the solid catalytic component and the results of the polymerization tests have been reported in Table III.

Comparative Example 4

Example 19 was repeated but using as ester ethylbenzoate as reported in Table III.

The X-ray spectrum of that catalytic component was similar to those of Examples 1—10. The characteristics of the solid product and the results of the polymerization test have been reported in Table III.

Examples 27—29

It was repeated Example 1, but using a solid catalytic component prepared according to Example 1 of German Pat. Appl. 3,022,738, wherein, instead of ethylbenzoate, esters of phthalic acid, listed in Table IV, were used and the treatment with $TiCl_4$ was effected at 120°C .

The X-ray spectrum of the catalytic components was similar to those of Examples 1—10.

The type of ester and the ratios have been reported in Table IV.

The working conditions and the results of the polymerization tests have been reported in Table IV.

Comparative Example 5

Example 27 was repeated but using a solid catalytic component prepared according to Example 1 of German Pat. Appl. 3,022,738.

The working conditions and the results of the polymerization test have been reported in Table 3.

Examples 30—34

Example 8 was repeated using instead of phenyltriethoxysilane an equimolecular amount of the alkoxysilanes reported in Table V.

The characteristics of the catalytic components and the results of the polymerization tests have been reported in Table V.

TABLE I

Example No.	Ester	Solid catalytic component			Polymerization					
		MgCl ₂ ester grinding mols/mols	Ti content of solid component % by weight	Surface area m ² /g	Al(C ₂ H ₅) ₃		Catalyst mg	Yield g polymer	I.I. %	η in h dl/g
					PES mols/mols					
1	diisobutyl-2,3-naphthalen-dicarboxylate	14	2.3	—	10	10	35	7,750	92.7	1.1
2	di-2-ethyl-hexyl-maleate	14	1.8	296	10	10	25	6,600	94	1.1
3	diisobutyl/maleate	14	2.9	—	10	10	54	5,700	92.2	1.2
4	isobutylacetate	7	3.2	—	10	10	32	5,700	91.2	1.8
5	isobutylpivalate	7	2.6	—	10	10	22	9,700	92.9	1.3
6	diethyl diisobutyl-malonate	14	2.4	—	10	10	47	4,750	94.3	1.7
7	di-n-butylphthalate	14	2.6	—	20	20	35	9,600	91.2	1.3
8	diisobutylphthalate	14	2.4	350	20	20	36	16,100	91.8	1.3
9	diisobutylphthalate	14	2.4	350	10	10	38	13,200	95.5	1.2
10	di-2-ethylhexylsebacate	14	2.3	—	10	10	52	4,500	94.8	1.2
11	di-isobutyl-phthalate	8	3.0	—	10	10	17	15,000	97.5	1.6
12	di-isobutyl-phthalate	8	1.4	21.8	10	10	14	7,000	97.2	1.5
comp. 1	ethylbenzoat	7	2.0	266	10	10	46	6,000	90.6	1.4
comp. 2	ethylbenzoate	7	2.0	266	5	5	47	4,000	92.7	1.6
comp. 3	ethylbenzoate	7	1.5	—	3.33	3.33	60	2,400	91.3	1.2

TABLE II

Example No.	Ester	Solid catalytic component			Polymerization						
		MgCl ₂ ester grinding mols/mols	Ti content of solid component % by weight	Surface area m ² /g	Al(C ₂ H ₅) ₃		Catalyst mg	Yield g polymer		I.I. %	η in h dl/g
					PES mols/mols			g catalyst component			
13	diphenylcarbonate	8	2	—	—	10	29	6,050	93.2	1.5	
14	1,2-didroxy-diacetate benzene	6	1.3	—	—	10	41	6,100	92.1	1.4	
15	ethyl-diphenylacetate	5	1.9	—	—	10	38	6,400	91.1	1.2	
16	diisobutyl-phthalate	7	1.4	157	157	20	19	9,100	98	1.3	
17	diisobutyl-phthalate	7	1.4	157	157	100	20	9,000	94.3	1.1	
18	isobutyl-benzoylacetate	7	2.1	—	—	10	42	5,900	95.4	1.2	

TABLE III

Example No.	Ester	Solid catalytic component		Polymerization				
		Ti content of solid component % by weight	Al(C ₂ H ₅) ₃	PES mols/mols	Catalyst mg	Yield g polymer	I.I. %	η in h dl/g
19	dioctylphthalate	2.7	20	20	19	12,100	92.2	1.8
20	diisobutylphthalate	2.4	20	20	22	13,900	96.9	1.2
21	dineopentylphthalate	3.5	20	20	15	18,500	97	1.2
22	diphenylphthalate	2.6	10	10	25	11,000	94.5	1.8
23	diethyl-butylmalonate	3.9	10	10	29	12,800	93.3	1.7
24	benzyl butylphthalate	3.1	20	20	24	14,000	96.1	1.4
25	mono-2-ethyl-hexylmaleate	2.8	10	10	50	8,000	92.5	1.3
26	monoisobutylphthalate	3.1	10	10	24	10,000	94.3	1.6
comp. 4	ethylbenzoate	3.8	5	5	38	6,850	91.5	1.5

TABLE IV

Example No.	Solid catalytic component				Polymerization				
	Ester	MgCl ₂ ester grinding mols/mols	Ti content of solid component % by weight	Al(C ₂ H ₅) ₃ PES mols/mols	Catalyst mg	Yield g polymer	I.I. %	η in h dl/g	
27	diethylphthalate	4.7	1.9	20	27	12,000	93.9	1.5	
28	isobutylphthalate	4.7	3.8	20	32	10,000	96.5	1.4	
29	neopentylphthalate	9.4	1.9	20	30	12,800	97.8	1.0	
comp. 5	ethylbenzoate	5	3.1	10	49	7,900	94.2	1.5	

TABLE V

Polymerization						
5	Example No.	Alkoxysilane	Catalyst mg	Yield	I.I. %	η in h dl/g
				g polymer		
10				g catalyst component		
	30	ethyltriethoxysilane	33.4	11,000	89.3	1.2
	31	chlorophenyldiethoxysilane	44.6	9,800	91.0	1.3
15	32	diphenyldiethoxysilane	25.1	14,300	92.4	1.0
	33	phenyldiethoxysilane	31.2	13,200	91.5	1.3
20	34	diphenyldimethoxysilane	22.2	18,200	93.1	1.5

Claims

1. A solid component of catalysts for the polymerization of alpha-olefins, comprising an anhydrous Mg-dihalide in active form as essential support, and supported on said dihalide a Ti-compound and an electron-donor compound characterized in that the Ti-compound is selected from Ti-halides or Ti-haloalcoholates and the electron-donor compound is an ester selected from the following groups of compounds:

1.1 Mono and polyesters of saturated polycarboxylic acids wherein at least one of the esteric carbonyl groups is linked to a tertiary or quaternary carbon atom or to a linear or branched chain of at least 4 carbon atoms;

1.2 Mono and polyesters of unsaturated polycarboxylic acids wherein at least two carboxy groups are linked to vicinal double bond-forming carbon atoms and in which at least one of the R hydrocarbyl radicals of the —COOR groups is a branched saturated or unsaturated radical with 3 to 20 carbon atoms or is an aryl or arylalkyl radical with 6 to 20 carbon atoms.

1.3 Mono and diesters of aromatic bicarboxylic acids having the COOH groups in ortho position and wherein at least one of the R hydrocarbyl radicals of the COOR groups contains from 3 to 20 carbon atoms;

1.4 Mono and polyesters of aromatic hydroxy compounds containing at least two hydroxyl groups in ortho position;

1.5 Esters of aromatic hydroxy acids wherein at least a hydroxyl group is in ortho position to the carboxy group;

1.6 Esters of saturated or unsaturated carboxylic acids wherein at least one of the R, R' hydrocarbyl radicals of the R COOR' groups is a saturated or unsaturated branched radical containing from 3 to 20 carbon atoms or is an arylalkyl radical with 7 to 20 carbon atoms or R is an aryl radical with 3 to 20 carbon atoms and in which when the R' radical is a linear hydrocarbyl radical, it contains from 3 to 20 carbon atoms.

1.7 Esters of carbonic acid of formula CO(OR)₂ in which at least one of the R radicals, which can be the same or different, is a hydrocarbyl radical with 3 to 20 carbon atoms.

2. A solid component as defined in claim 1) in which the Mg dihalide is Mg dichloride or Mg dibromide, the Ti halide is a Ti tetrahalide and the ester is selected from the 1.2, 1.3, 1.6 and 1.7 groups.

3. Catalysts for the polymerization of alpha-olefins comprising the product of reaction of the following components:

a) an Al-trialkyl or an Al-alkyl compound containing 2 or more Al atoms linked to each other through an oxygen or nitrogen atom or through SO₄ or SO₃ groups;

b) a silicon compound containing one or more Si—OR, Si—OCOR or Si—NR₂ bond, R being a hydrocarbyl radical;

c) a solid component as defined in claims 1) to 2); the molar ratio of component b) with respect to the halogenated Ti-compound supported on component c) being of at least 1, and with respect to the Al-alkyl compound less than 20.

4. Catalysts as defined in claim 3) in which the silicon compound of component b) is a phenyl di- or trialkoxysilane or an alkyl di- or trialkoxysilane.

5. Catalysts as defined in claim 4) in which the component c) is the solid component as defined in claim 2).

6. Process for the polymerization of alpha-olefins CH₂=CHR in which R is an alkyl radical with 1 to 4 C,

or an aryl radical and mixtures of said olefins with ethylene, characterized in that the polymerization process is carried out in liquid phase in presence or not of an inert hydrocarbon solvent or in gas phase in presence of a catalyst as defined in claims 3) to 5).

5 Patentansprüche

1. Feste Katalysator-Komponente zur Polymerisation von α -Olefinen, umfassend ein wasserfreies Magnesiumdihalogenid in aktiver Form als wesentlichen Träger und aufgebracht auf das genannte Dihalogenid eine Titanverbindung und eine Elektronen-Donor-Verbindung, gekennzeichnet dadurch, daß die Titanverbindung ein Titanhalogenid oder Titanhaloalkoholat und die Elektronen-Donor-Verbindung ein Ester, ausgewählt aus folgenden Verbindungsgruppen, ist:

1.1 Mono- und Polyester von gesättigten Polycarbonsäuren, worin wenigstens eine der Estercarbonylgruppen an ein tertiäres oder quartäres Kohlenstoffatom oder an eine geradkettige oder verzweigte Kohlenstoffkette von wenigstens 4 Kohlenstoffatomen gebunden ist;

1.2 Mono- und Polyester von ungesättigten Polycarbonsäuren, worin wenigstens zwei Carboxylgruppen an vicinale Doppelbindungs-bildende Kohlenstoffatome gebunden sind und in welchen wenigstens einer der Kohlenwasserstoffreste R der —COOR -Gruppen ein verzweigter, gesättigter oder ungesättigter Rest mit 3 bis 20 Kohlenstoffatomen oder ein Aryl- oder Arylalkylrest mit 6 bis 20 Kohlenstoffatomen ist;

1.3 Mono- und Diester von aromatischen Dicarbonsäuren, welche die COOH -Gruppen in ortho-Stellung tragen und worin wenigstens einer der Kohlenwasserstoffreste R der COOR -Gruppen 3 bis 20 Kohlenstoffatome enthält;

1.4 Mono- und Polyester von aromatischen Hydroxyverbindungen mit wenigstens zwei Hydroxylgruppen in ortho-Stellung;

1.5 Ester von aromatischen Hydroxysäuren, worin wenigstens eine Hydroxylgruppe in ortho-Stellung zur Carboxylgruppe ist;

1.6 Ester von gesättigten oder ungesättigten Carbonsäuren, worin wenigstens einer der Kohlenwasserstoffreste R der R COOR' -Gruppen ein gesättigter oder ungesättigter, verzweigter Rest mit 3 bis 20 Kohlenstoffatomen oder ein Arylalkyl-Rest mit 7 bis 20 Kohlenstoffatomen oder R ein Aryl-Rest mit 3 bis 20 Kohlenstoffatomen ist und, falls der Rest R' ein unverzweigter Kohlenwasserstoffrest ist, 3 bis 20 Kohlenstoffatome enthält;

1.7 Ester der Kohlensäure der Formel CO(OR)_2 , in welchen wenigstens einer der Reste R, welche gleich oder verschieden sein können, ein Kohlenwasserstoffrest mit 3 bis 30 Kohlenstoffatomen ist.

2. Fest Komponente gemäß Anspruch 1, in welcher das Magnesiumdihalogenid entweder Magnesiumdichlorid oder Magnesiumdibromid, das Titanhalogenid ein Titanetrahalogenid ist und der Ester Verbindungen der Unterpunkte 1.2, 1.3, 1.6 und 1.7 entspricht.

3. Katalysatoren zur Polymerisation von α -Olefinen, umfassend die Reaktionsprodukte der folgenden Bestandteile:

a) eine Aluminiumtrialkyl- oder eine Aluminiumalkyl-Verbindung, welche zwei oder mehr Aluminiumatome enthält und durch ein Sauerstoff- oder Stickstoffatom oder durch SO_4 - oder SO_3 -Gruppen verbunden sind;

b) eine Siliciumverbindung, welche eine oder mehrere Si—OR -, Si—OCOR - oder Si—NR_2 -Bindungen enthält, worin R ein Kohlenwasserstoffrest ist;

c) eine feste Komponente gemäß den Ansprüchen 1 und 2, worin das molare Verhältnis der Komponente b) bezüglich der halogenierten Titanverbindung, die auf Komponente c) aufgebracht ist, wenigstens 1 und bezüglich der Aluminiumalkylverbindung weniger als 20 beträgt.

4. Katalysatoren gemäß Anspruch 3, in welchen die Siliciumverbindung des Bestandteils c) ein Phenylidi- oder -trialkoxysilan oder ein Alkyldi- oder trialcoxysilan ist.

5. Katalysatoren gemäß Anspruch 4, in welchen die Komponente c) eine feste Komponente gemäß Anspruch 2 ist.

6. Verfahren zur Polymerisation von α -Olefinen $\text{CH}_2=\text{CHR}_2$, in welchen R ein Alkylrest mit 1 bis 4 Kohlenstoffatomen oder ein Arylrest ist und von Mischungen der genannten Olefine mit Ethylen, gekennzeichnet dadurch, daß das Polymerisationsverfahren in einer flüssigen Phase mit oder ohne einem inerten Kohlenwasserstoff-Lösungsmittel oder in Gasphase in Gegenwart eines Katalysators gemäß der Ansprüche 3 bis 5 durchgeführt wird.

Revendications

1. Un composant solide de catalyseurs destiné à la polymérisation des alpha-oléfinés, comprenant un dihalogénure de magnésium anhydre sous forme active comme support essentiel, et maintenus sur ledit dihalogénure un composé de titane et un composé électrodonneur, caractérisé en ce que le composé de titane est choisi parmi les halogénures de titane ou les haloalcooolates de titane et le composé électrodonneur est un ester choisi dans les groupes de composés suivants:

1.1 Mono et polyesters des acides polycarboxyliques saturés dans lesquels l'un au moins des groupes

carbonés de l'ester est lié à un atome de carbone tertiaire ou quaternaire, ou à une chaîne linéaire ou ramifiée comportant au moins 4 atomes de carbone;

1.2. Mono et polyesters des acides polycarboxyliques insaturés dans lesquels deux au moins des groupes carboxy sont liés aux atomes de carbone vicinaux formant une double liaison et dans lesquels au moins l'un des radicaux hydrocarbonés R des groupes —COOR est un radical ramifié saturé ou insaturé comportant 3 à 20 atomes de carbone ou est un radical aryle ou arylalkyle comportant de 6 à 20 atomes de carbone;

1.3. Mono et diesters des acides bicarboxyliques aromatiques comportant des groupes COOH en position ortho et dans lesquels l'un au moins des radicaux hydrocarbonés R des groupes COOR comporte de 3 à 20 atomes de carbone;

1.4. Mono et polyesters de composés aromatiques hydroxylés comportant au moins deux groupes hydroxyles en position ortho;

1.5. Esters des acides aromatiques hydroxylés dans lesquels au moins un groupe hydroxyle est en position ortho par rapport au groupe carboxy;

1.6. Esters des acides carboxyliques saturés ou insaturés dans lesquels au moins l'un des radicaux hydrocarbonés R et R' des groupes RCOOR' est un radical ramifié saturé ou insaturé contenant de 3 à 20 atomes de carbone, ou est un radical arylalkyle comportant de 7 à 20 atomes de carbone, ou bien R est un radical aryle comportant de 3 à 20 atomes de carbone et qui contient de 3 à 20 atomes de carbone lorsque le radical R' est un radical hydrocarboné linéaire;

1.7. Esters de l'acide carbonique de formule CO(OR)₂ dans lesquels l'un au moins des radicaux R, qui peuvent être identiques ou différents est un radical hydrocarboné comportant de 3 à 20 atomes de carbone.

2. Un composant solide selon la revendication 1, dans lequel le dihalogénure de magnésium est le dichlorure de magnésium ou le dibromure de magnésium, l'halogénure de titane est un tétrahalogénure de titane et l'ester est choisi dans les groupes 1.2, 1.3, 1.6 et 1.7.

3. Catalyseurs destinés à la polymérisation des alpha-oléfinas comprenant le produit de la réaction des composants suivants:

a) un composé trialkylaluminium ou alkylaluminium comportant 2 atomes d'aluminium ou davantage, reliés entre eux par l'intermédiaire d'un atome d'oxygène ou d'azote ou par l'intermédiaire de groupes SO₄ ou SO₃;

b) un composé de silicium contenant une ou plusieurs liaisons Si—OR, Si—OCOR ou Si—NR₂, R étant un radical hydrocarboné;

c) un composant solide selon les revendications 1 ou 2, le rapport molaire du composant b) par rapport au composé de titane halogéné supporté par le composant c) étant au moins égal à 1, et, par rapport au composé alkylaluminium, étant inférieur à 20.

4. Catalyseurs selon la revendication 3, dans lesquels le composé de silicium du composant b) est un phényldi- ou trialkoxysilane ou un alkyl-di- ou trialkoxysilane.

5. Catalyseurs selon la revendication 4, dans lesquels le composant c) est le composant solide selon la revendication 2.

6. Procédé de polymérisation des alpha-oléfinas CH₂=CHR dans lesquelles R est un radical alkyle comportant de 1 à 4 atomes de carbone ou un radical aryle et des mélanges desdites oléfines avec l'éthylène, caractérisé en ce que le procédé de polymérisation est effectué en phase liquide en présence ou non d'un solvant hydrocarboné inerte ou en phase gazeuse en présence d'un catalyseur selon les revendications 3 à 5.